The infrared and ultraviolet absorption spectra of laboratory-produced carbon dust: evidence for the presence of the C_{60} molecule

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In carbon smoke samples prepared from vaporized graphite at elevated quenching gas pressures (e.g. > 100 Torr He) new absorption features have been observed in the infrared (the strongest at 1429, 1183, 577, and 528 cm^{-1}). Broader features also have been observed in the ultraviolet (the strongest at 340, 270, and 220 nm). By studying ^{13}C-enriched samples we have shown that the infrared absorptions are produced by large, pure carbon molecules. The evidence supports the idea that the features are produced by the icosahedral C_{60} molecule.

1. Introduction

The C_{60} molecule was discovered as a peak in the mass spectra of quenched carbon vapor [1,2]. In order to explain the stability of this molecule, Kroto et al. [2] proposed the highly symmetric soccer-ball-like molecular shape, coined Buckminsterfullerene (a truncated icosahedron with point group I_h). Because of its unusually high symmetry C_{60} is expected to have only four infrared active vibrational modes (of species T_{1u}) which calculations have shown are expected to occur at about 1600 ± 200, 1300 ± 200, 630 ± 100, and 500 ± 50 cm^{-1} [3–6], the spread indicating the author-to-author variation in the calculated line positions. The presence of strong electronic transitions at 260 nm and shorter wavelengths has also been predicted [7]. Several authors have commented on the importance of producing enough C_{60} for carrying out absorption spectroscopy, but so far the only known absorption feature is a weak electronic transition detected by depletion spectroscopy at 386 nm [8]. In order to further confirm the existence of the soccer-ball-shaped molecule and to investigate its role in both interstellar and terrestrial chemistry, knowledge of its absorption spectra is vitally needed.

We have recently reported the discovery of four strong lines in the infrared and three broader features in the near ultraviolet, observed in absorption spectra of laboratory-produced carbon smoke [9]. The infrared lines have also been noticed by other investigators [10]. The aim of this communication is to report new spectroscopic results on isotopically modified samples which support the idea that the reported features in fact originate from a pure and massive carbon molecule which very likely is the soccer-ball-shaped C_{60} molecule.

2. Experimental procedures and results

Carbon smoke particles were produced by evaporating graphite rods by resistive heating in a conventional glass bell jar evaporator filled with an inert quenching gas. The carbon vapor nucleates in the presence of an inert quenching gas to form smoke particles, which can be collected on substrates. In order to produce ^{13}C dust particles, we made rods from commercially available, isotopically enriched carbon powder. In making the rods the powder was compressed (at about 1 kbar) and heated (to about 1300°C) for a few minutes within a quartz-glass tube.

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The smoke produced by vaporizing the rods was collected either on transparent substrates for transmission measurements or on gold-coated glass surfaces for reflection measurements. The latter method avoids the complicating interference fringes that arise from transparent substrates when spectra are taken at high resolution. It also avoids unwanted substrate absorptions. Infrared measurements were made with an FTIR spectrometer (Bruker 113V) at 2 or 0.3 cm^{-1} resolution, and visible–ultraviolet measurements (in the range shortward of 600 nm) were taken with grating instrument (PE-330) at 2 nm resolution.

The spectra from carbon dust obtained from natural carbon (about 99% ^{12}C) are shown in fig. 1. At pressures of about 10 Torr, the infrared spectra consist of a featureless background which steadily rises towards shorter wavelengths. Broad humps at 1600–1200 cm^{-1} and 900–500 cm^{-1} are superimposed on this rise. These humps originate from stretching and bending modes of carbon within the highly distorted graphite structure of the dust particles. Infrared features which have been observed at 1588 and 868 cm^{-1} only in highly oriented single crystals of graphite [11] are absent in our spectra. In overall shape, our spectra are very similar to those published in the literature [12]. However, for samples produced at higher quenching gas pressures (100 Torr for example), we noticed four prominent peaks which emerge out of the essentially unchanged continuum, along with a number of weaker lines. Also, in the ultraviolet, new features appear which seem to be correlated with the new infrared features. The infrared spectrum obtained with 99% ^{13}C at the same quenching gas pressure shows that the four strong bands, as well as a number of the weaker lines, are displaced by a constant fraction (0.9625). This value is almost precisely the square root of the ratio of the ^{12}C to the ^{13}C masses, as expected for pure carbon.

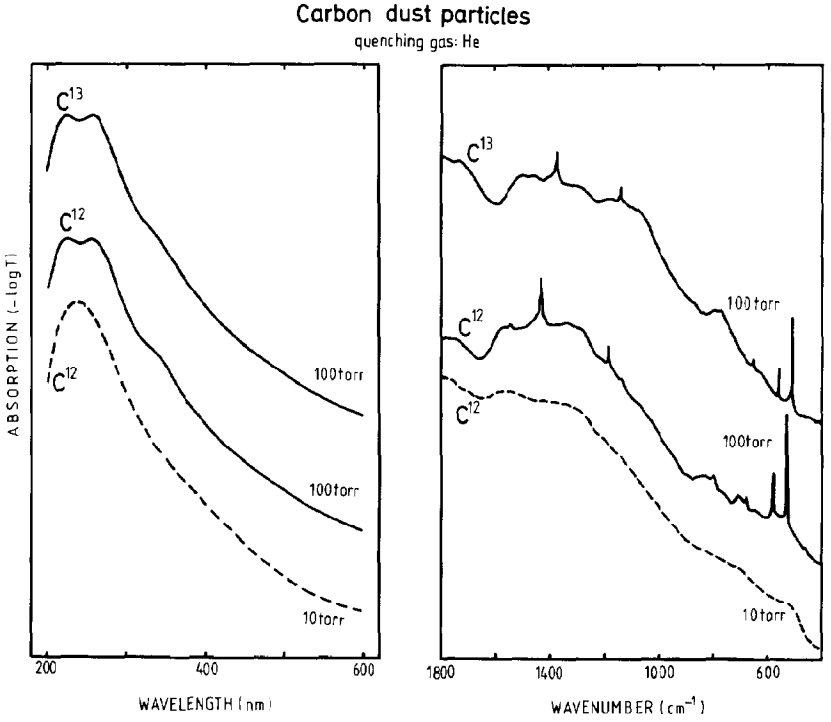

Fig. 1. The ultraviolet, visible, and infrared spectra of laboratory-produced carbon dust particles produced using different quenching gas pressures and isotopic compositions (99% ^{12}C or ^{13}C respectively). As an evaluation of the displacement of the infrared lines in ^{13}C samples shows, the carrier of the infrared features which appear at higher quenching gas pressures must be a pure carbon molecule. For clarity, the spectra are vertically displaced.

Table 1
The infrared line positions (rounded to full wavenumbers) and integrated strength of lines which show similar frequency ratios in ^{12}C and ^{13}C dust samples. For the weaker features, this list is not complete

Obs. freq. 99% ^{12}C (cm^{-1})	Obs. freq. 99% ^{13}C (cm^{-1})	Relative intensity	Width 99% ^{12}C (cm^{-1})	Width 90% ^{13}C (cm^{-1})
1429	1375	100	9.2	15.8
1183	1138	20	4.6	6.2
796	765	4		
675	649	6		
643	619	3		
577	556	20	3.3	4.0
565	545	3		
536	516	4		
528	508	70	3.0	3.5

This is strong evidence that the line carriers in our spectra are pure carbon molecules. Table 1 lists the observed IR line positions for the 99% ^{12}C and ^{13}C cases.

The UV spectra for 100 Torr quenching gas pressure and different isotopic compositions remain essentially unchanged. The extra features maintain their positions at 340, 270, and 220 nm (fig. 1). It was observed that the three ultraviolet features and the four infrared lines always appear together and form a characteristic pattern which is not intensity correlated with the background continuum. Thus the infrared and ultraviolet features both appear to originate from a new carbon species which is formed at higher gas pressures along with the dust which produces the continuum. The appearance of new spectral features in our experiments as the quenching gas pressure is increased is reminiscent of the appearance of the strong C_{60} peak in the mass spectra of the previous experiments [2] when the vaporizing laser pulse was timed to occur at the maximum density of the He quenching gas pulse.

Infrared spectroscopy performed at 0.3 cm^{-1} resolution on 90% ^{13}C samples displayed an increased line width for all the four main features but no essential change in the line shapes. Table 1 lists the observed widths. For a light carbon molecule one would expect line broadening caused by the various possible isotopic modifications (isotopomers) of the molecule. Instead we noted that the increase in linewidth (e.g. for the 528 cm^{-1} feature) is rather limited. It thus appears from these data that the carrier of the infrared features is a quite large molecule or group of large molecules.

In addition to the four strong infrared bands, table 1 lists five weak bands which also show the isotope shifts expected of pure carbon. There may also be more weaker bands. It is possible that these may also arise from the same C_{60} molecule, but with its symmetry disturbed by the carbon impurity mass present in approximately 1% abundance. The disturbed symmetry may be causing some disallowed modes to become observable. Other symmetry distortions may occur by interaction of C_{60} with the carbon grains. One may also speculate on the possibility that these additional bands are from the C_{70} molecule, which appears to a lesser extent in the mass spectra under conditions that produce a strong C_{60} peak [2].

In a search of the spectral range from about 100 to 5000 cm^{-1}, as well as in the near infrared and visible, we detected no other features. Based on the ratio of absorption strengths in the infrared lines to the infrared continuum one can estimate that the abundance of the C_{60} molecule is of the order of 1% of the total sample.

3. Conclusions

Correlated absorption features in the ultraviolet and in the infrared, which were recently reported for the first time in our previous work, appear to be caused by pure carbon in view of the isotope shift observed in the infrared spectra. The number of strong bands in the vibrational region of the infrared is four, which agrees in number with that predicted by the symmetry of the soccer-ball-shaped C_{60} molecule. Vibrational frequencies noted in this paper are also in acceptable agreement with published theoretical values. The ultraviolet features are in rough agreement with the expected absorption frequencies of the same C_{60} molecule. We also note a qualitative correspondence between the high quenching gas pressure required to produce our newly observed bands and the high entraining gas pressure and relatively long clustering times involved in the previous mass spectrometric works. For these reasons we believe we have produced the first reported sample of Buckminsterfullerene in sufficient quantities for

doing infrared and ultraviolet absorption spectroscopy. For future studies of the properties of C_{60} it may be possible to extract bulk quantities of this molecule from smoke samples.

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